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Spectroscopy and Kinetics of Singlet Perfluoro-4-biphenylnitrene and Singlet Perfluorophenylnitrene

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Laser flash photolysis (LFP) of perfluorophenyl azide and perfluoro-4-biphenyl azide produces the corresponding singlet nitrenes which were detected by their transient absorptions at 330 and 350 nm, respectively. The absolute rate constants of the fundamental processes that consume the singlet nitrenes (intersystem crossing, k_{isc}, rearrangement, k_{R}; reaction with pyridine, k_{pyr}) were determined by monitoring the decay of the singlet nitrene and by the growth of its reaction products (ketenimine, triplet nitrene, or pyridine ylide). In the case of singlet 4-perfluorobiphenylnitrene in CH_2Cl_2 $k_{\mathrm{isc}} = (2.2 \pm 0.1) \times 10^6\ \mathrm{s}^{-1}$, $k_{\mathrm{R}} = 10^{13.2\pm0.2} \exp[-(9400 \pm 400)/RT]\ \mathrm{s}^{-1}$, and $k_{\mathrm{pyr}} = 10^{9.06\pm0.15} \exp[-(2400 \pm 200)/RT]\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$. In the case of singlet perfluorophenylnitrene in CH_2Cl_2 $k_{\mathrm{isc}} = (1.05 \pm 0.05) \times 10^7\ \mathrm{s}^{-1}$, $k_{\mathrm{R}} = 10^{13.8\pm0.3} \exp[-(8800 \pm 400)/RT]\ \mathrm{s}^{-1}$, and $k_{\mathrm{pyr}} = 10^{9.00\pm0.13} \exp[-(1600 \pm 160)/RT]\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$.

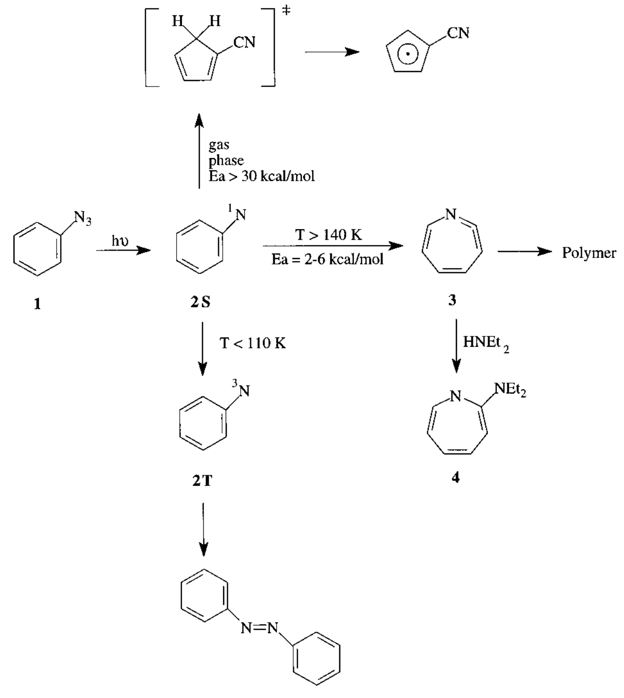
I. Introduction

A unified picture of the photochemistry of simple aryl azides has been pieced together from data generated in several laboratories.[1] Photolysis of phenyl azide **1** releases singlet phenylnitrene **2S** whose fate depends on temperature and phase. In the gas phase, **2S** cannot shed its excess energy and rearranges over a large barrier to form cyanocyclopentadiene, the global minimum on the C_6H_5N surface. This species is also formed with excess vibrational energy and fragments in the gas phase to cyanocyclopentadienyl radical. The absorption and emission spectra of this radical have been obtained and analyzed.[2] These spectra were originally misassigned to triplet phenylnitrene[3].

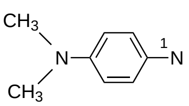
In solution phase, **2S** rapidly sheds its excess energy and ring expands over a small (2−6 kcal/mol)[4,5] barrier to form ketenimine **3**. We have consistently written this as a one-step process (as shown in Schemes 1 and 2), but recent calculations of Borden and Karney indicate that this is a two-step process (Scheme 3) with the slow step being the formation of an azirine (**5**) intermediate.[6] At cryogenic temperatures, **2S** preferentially relaxes[4] to the lower energy (17 kcal/mol)[7] triplet state of the nitrene.

Perfluorination dramatically raises the barrier to rearrangement of the aryl nitrene (Scheme 2).[1,6,8,9] Photolysis of azide **6** generates singlet nitrene **7S**, which we have deduced[1,8,9] must surmount a 7−9 kcal/mol barrier to rearrange and eventually form ketenimine **8**.[10] This sufficiently extends its lifetime to allow its trapping with external reagents such as pyridine to form adducts (e.g., ylide **9**). The ylide is an isolable compound whose strong absorption maximum at 390 nm makes it an ideal probe of the dynamics of the singlet nitrene.[1,8,9]

SCHEME 1

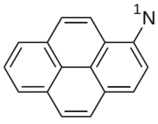


Despite this progress, direct observations of singlet arylnitrenes are exceedingly rare. Only the singlet states of (*p*-(dimethylamino)phenylnitrene **10** and 1-pyrenylnitrene **11** have been reported,[11,12] and these reports were of a preliminary nature.



10

λ_{max} = 460 nm
τ(298) = 120 ps



11

λ_{max} = 450 nm
τ(298) = 22 ns

Miura and Kobayashi[13] have studied 4,4′-biphenyl bisazide in solution by LFP methods. They have concluded that photolysis leads to extrusion of a single molecule of nitrogen

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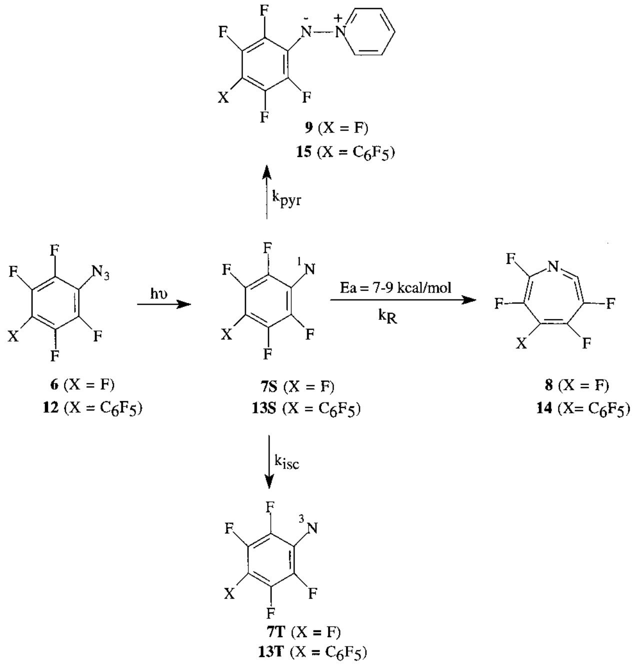
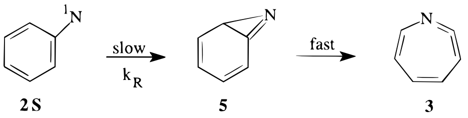
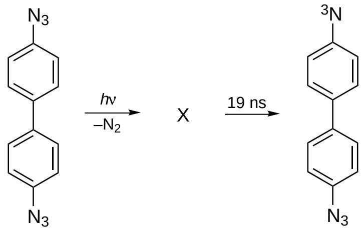
SCHEME 2



SCHEME 3



with the formation of a singlet state species, “X”, with a lifetime of 19 ns.



These workers did not specify the nature of X. This species absorbs at 380 nm and its spectrum is similar to that reported for dehydroazepines.[1,4]

Herein we are pleased to report our studies of perfluoro-4-biphenyl azide **12** (Scheme 2) and new studies of perfluorophenyl azide **6** with improved time resolution. These have led to spectroscopic characterization of singlet nitrene **13** (Scheme 2, X = C_6F_5) and measurement of the kinetics of singlet nitrenes **7S** and **13S** as a function of temperature. This has revealed the absolute values of k_{isc}, k_R, and k_{pyr} and the Arrhenius parameters of the latter two processes of both singlet nitrenes. The results are in good agreement with conclusions deduced from indirect analysis of the photochemistry of perfluorbiphenyl azide **6** and simple para-substituted derivatives.[7,8,14]

II. Results

Perfluorobiphenylnitrene. Azide **12** was studied by laser flash photolysis (LFP) techniques (Nd:YAG laser, 35 mJ, 355 nm, 0.15 ns fwhm or XeCl excimer laser, 308 nm, 100 mJ, fwhm 15 ns) in methylene chloride. LFP of **12** produces transient spectra which were recorded immediately after the laser flash (Figure 1a, curve 1) and 2 μs after the laser pulse (Figure 1, curve 2). There is a large sharp peak at 350 nm (Figure 1a) which decays within 1 μs. Expansion of the transient absorption spectra (Figure 1b) reveals that there is a weaker, broader absorption around 500 nm which also decays rapidly.

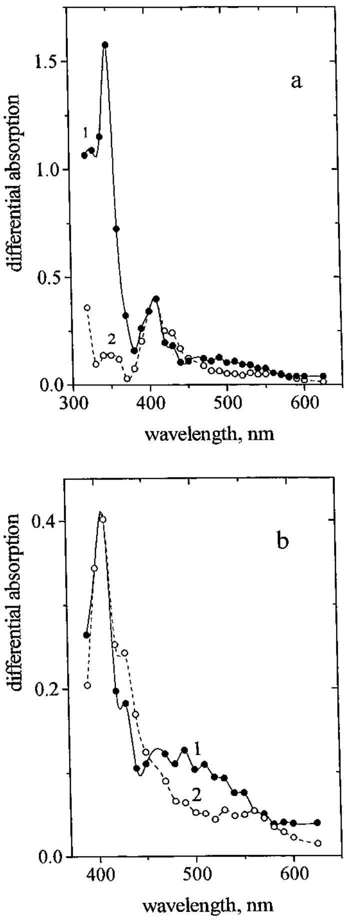


Figure 1. Transient spectra (a) obtained by LFP (308 nm excimer, 15 ns) of perfluorobiphenyl azide **12** recorded immediately after the laser pulse (●) and 2 μs after the laser pulse (○). An extended presentation (b).

The transient absorptions at 350 and 510 nm decay exponentially with observed rate constants of (4.6 ± 0.5) × 10^6 and (4.1 ± 0.5) × 10^6 s^{-1}, respectively (Figure 2), at 24 °C. There is an immediate increase in transient absorption at 430 nm, following LFP, followed by an exponential increase in absorption (k_{obs} = (4.1 ± 0.4) × 10^6 s^{-1}). There is an isosbestic point at 460 nm. Laser flash photolysis of **12** leads to an immediate transient absorption followed by no further change in transient absorption at this wavelength.

The simplest interpretation is that a single species absorbs between 325 and 600 nm and has a lifetime of about 250 ns. This intermediate decays to a mixture of secondary species which also absorb in the same spectral region.

It is well-known that photolysis of aryl azides at 77 K in rigid, optically clear glasses produces the UV−vis spectra of triplet nitrenes.[1,4,15] Photolysis (313 nm) of azide **12** produces the persistent spectrum of Figure 3 (solid line). The low-temperature spectrum clearly resembles that of the second species (Figure 3, dashed line) produced upon LFP of perfluorobiphenyl azide **12**. The maximum at 440 nm (77 K) coincides with the shoulder of the larger absorption observed in solution at 420 nm. The 420 nm species is assigned to dehydroazepine.

It is tempting to assign the first formed species in solution (298 K) to singlet nitrene **13S** and the second species to triplet nitrene **13T** (Scheme 2) and dehydroazepine.[1,4,8] To test these

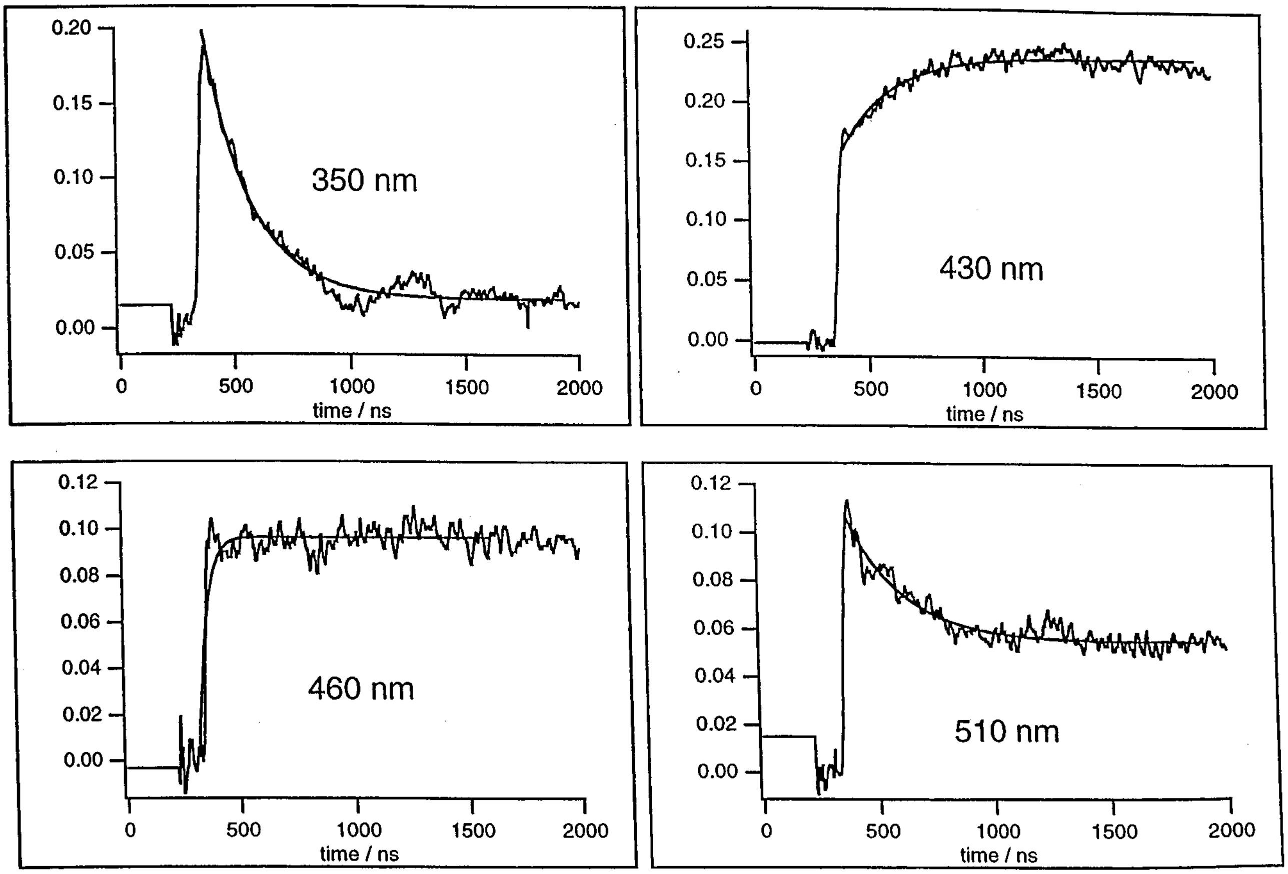


Figure 2. Changes in transient absorption at selected wavelengths with time following LFP (308 nm excimer, 15 ns) of perfluorobiphenyl azide **12**.

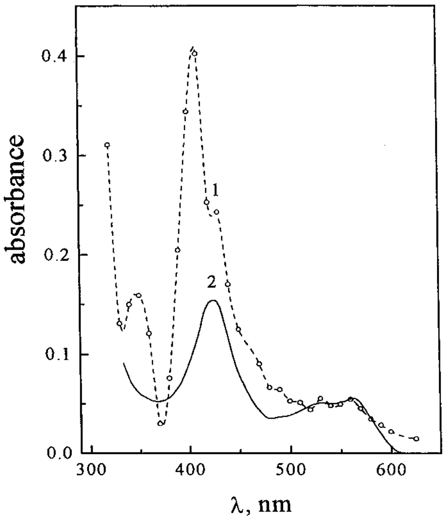


Figure 3. Persistent spectrum of triplet nitrene **13T** obtained by 313 nm photolysis of **12** in methylcyclohexane glass at 77 K (curve 2) and that detected 2 μs after LFP of **12** in CH_2Cl_2 at 295 K.

assignments, the photolysis was repeated in the presence of pyridine. Photolysis of perfluorophenyl azide **6** in the presence of pyridine forms isolable ylide **9**, which absorbs intensely at 390 nm.[8] Photolysis (313 nm, Hg arc lamp) of azide **12** in the presence of pyridine also produces an intensely absorbing, persistent, intermediate with $\lambda_{max} = 420$ nm (Figure 4). The rate of formation of ylide **15**, determined by LFP, is first order in the concentration of pyridine (Figure 5). The slope of this plot ((2.48 ± 0.17) × 10^7 M^{-1} s^{-1}, 298 K) is the absolute rate constant of reaction of singlet nitrene **13S** with pyridine (k_{pyr}).

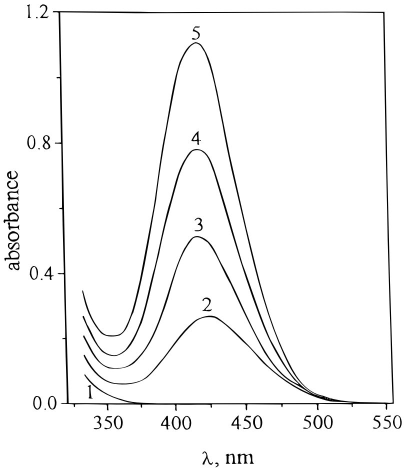


Figure 4. Absorption spectrum of ylide **15** produced by 313 nm photolysis [(1) 0, (2) 24, (3) 42, and (5) 67 s] of **12** in the presence of 1.04 M pyridine in CH_2Cl_2. Samples containing 0.013 M **12** and pyridine were deoxygenated by bubbling with argon.

The intercept of this plot ((4.2 ± 0.5) × 10^6 s^{-1}, 25 °C) is the total rate constant of decay ($k_{isc} + k_R$) of singlet nitrene **13S** in the absence of pyridine (Figure 5). The similarity in the rate constant of decay of the 350, 510 nm absorbing species and the species that reacts with pyridine to form an ylide leads us to confidently associate these two kinetic entities with singlet nitrene **13S**. The most accurate measurement of the lifetime of singlet nitrene **13S** is obtained in the absence of pyridine with monitoring of the singlet directly at 350 nm where the singlet nitrene absorbs most strongly.

The yield of ylide **15**, produced by 313 nm photolysis of **12**, as a function of pyridine concentration is given in Figure 6a.

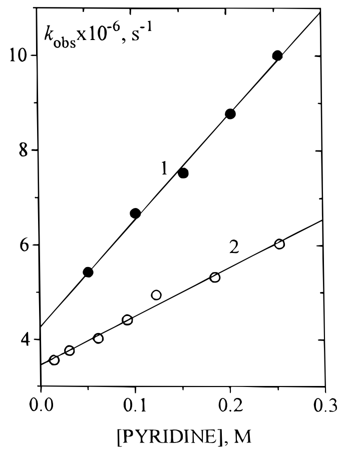


Figure 5. Plots of k_{obs} versus [pyridine] obtained by LFP (308 nm excimer, 15 ns) of **12** in CH_2Cl_2 at (1) 303 and (2) 255 K.

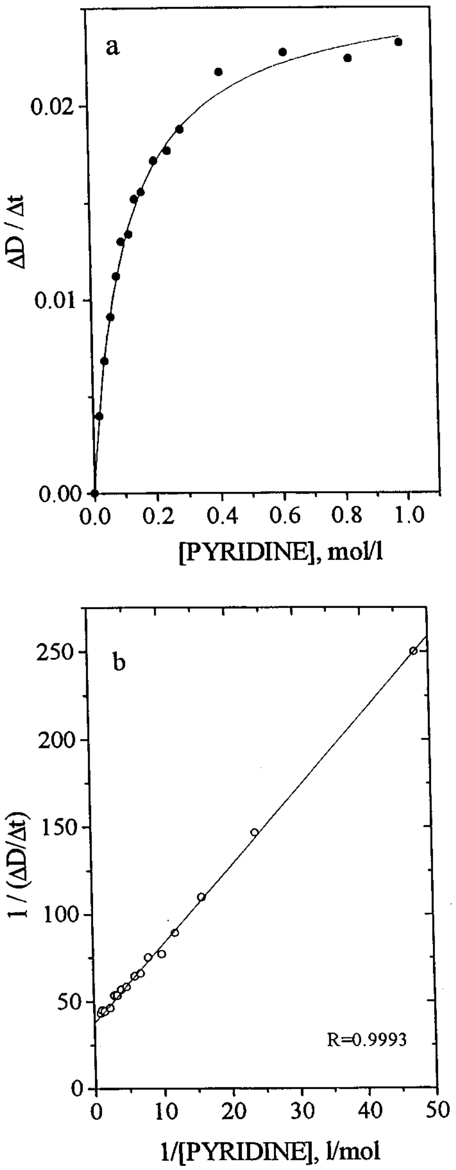


Figure 6. (a) Yield of ylide **15** produced upon continuous photolysis (Hg arc lamp, 313 nm) of **12** in CH_2Cl_2 at 25 °C and (b) a double-reciprocal treatment of these data.

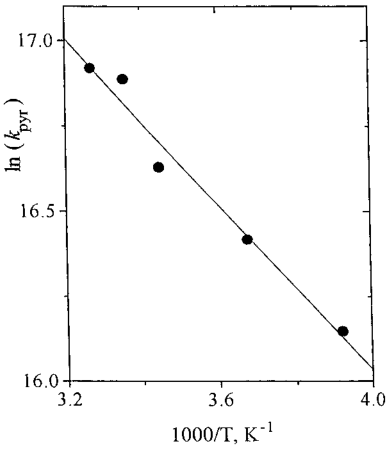


Figure 7. Arrhenius treatment of k_{pyr} with singlet nitrene **13T** and pyridine (308 nm excimer laser).

TABLE 1. Dependence of Lifetime of Singlet Perfluorobiphenylnitrene 13T with Variation of Solvent and Temperature ($T = -25$ and 21 °C)

solvent	τ, ns −25 °C	 21 °C	$k_{isc} \times 10^{-6}$, s^{-1} (±5%)	$k_R \times 10^{-6}$, s^{-1} (±5%)
C_5H_{12}	530 ± 20	259 ± 10	1.9	2.0
CH_2Cl_2	370 ± 20	254 ± 5	2.7	1.2
CH_3CN	325 ± 15	220 ± 3	3.1	1.4
CCl_3CN	430 ± 20	297 ± 6	2.3	1.1
CH_3OH	130 ± 3	65 ± 7	7.7	7.7
CH_3OD	151 ± 4	76 ± 2	6.6	6.6
CH_3CH_2OH	124 ± 4	≈50	8.1	11.9

$k_{isc}(CH_3OH)/k_{isc}(CH_3OD) = 1.16 \pm 0.06$

As predicted by Scheme 2, a double-reciprocal plot of these data is linear (Figure 6b).

The ratio of the intercept to the slope of this plot is 4.2, which can be equated to $k_{pyr}/(k_R + k_{isc})$. In previous studies,[8] a value of k_{pyr} of singlet nitrene **13S** was assumed and used to deduce values of k_R and k_{isc} by this type of analysis. A double-reciprocal analysis is less precise than that obtained by direct measurement ($k_{pyr}/(k_R + k_{isc}) = 5.9$), but still provides reasonable estimates of the carbene lifetime. Thus, the directly measured ratio of rate constants is consistent with past and presently determined double-reciprocal analyses.

The rate constant of reaction of singlet nitrene **13S** with pyridine was studied as a function of temperature. Arrhenius treatment of the data (Figure 7) indicates that the activation energy for this process is 2.4 ± 0.2 kcal/mol and that the preexponential factor is $10^{9.06\pm0.15}$ M^{-1} s^{-1}.

The lifetime of singlet nitrene **13S** was determined in a variety of solvents (Table 1) at −25 and +21 °C by monitoring the decay of the transient absorption at 520 nm. The decay of the singlet nitrene is slightly accelerated in the polar solvent acetonitrile relative to pentane. The singlet lifetime is dramatically shortened in methanol, an effect which has been observed previously with perfluorophenylnitrene **7S**.[8] This effect has been attributed to catalysis of nitrene intersystem crossing (ISC) via hydrogen bonding and stabilization of closed-shell configurations of the singlet aryl nitrene. Closed-shell singlets have greater spin−orbit coupling than open-shell singlets and will undergo ISC more rapidly. Both the rate of rearrangement (k_R) and intersystem crossing (k_{isc}) increase in the alcohol solvent. The $CH_3OH(D)$ kinetic isotope effect to the disappearance of **13T** is 1.16 at both 294 and 248 K and demonstrates the importance of the OH(D) bond in catalyzing intersystem crossing.

The dependence of the lifetime of singlet nitrene **13S** (monitored at 520 nm) was determined as a function of temperature in CH_2Cl_2. The results are shown in Figure 8. The rate constant of decay of **13S** decreases as the temperature is

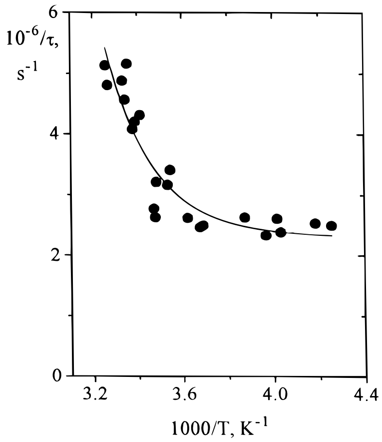


Figure 8. A plot of the rate constant of disappearance of singlet nitrene **13T** versus (1/*T*) determined at 520 nm (LFP, 308 nm excimer laser, 15 ns).

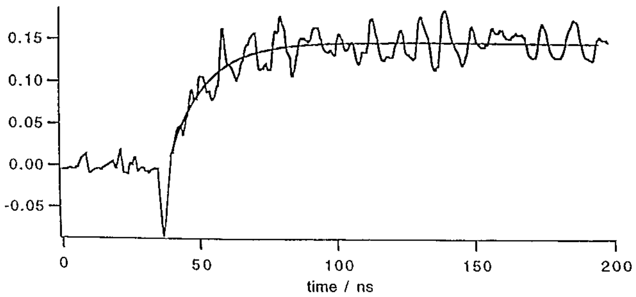


Figure 9. Formation of ylide **9** produced by LFP (355 nm, Nd:YAG laser, 150 ps) of perfluorophenyl azide **6** in CH_2Cl_2 containing 0.7 M pyridine at 21 °C.

reduced until about 0 °C, after which no further reduction in rate constant is realized. This results in a nonlinear Arrhenius plot. The temperature dependence of the observed rate constant of decay of **13S** (k_{obs}) can be fit to the equation below.

$$k_{obs} = (2.2 \pm 0.1) \times 10^6\ s^{-1} + 10^{13.2\pm0.2} \exp\left(-\frac{9400 \pm 400}{RT}\right)$$

where

$$k_{obs} = k_{isc} + k_R$$

These values can be immediately associated with the processes of Scheme 2 as $k_{isc} = (2.2 \pm 0.1) \times 10^6\ s^{-1}$ and $k_R = 10^{13.2\pm0.2}$ exp[−(9400 ± 400)/*RT*].

At room temperature, rearrangement of singlet nitrene **13S** and ISC proceeds with comparable rates in CH_2Cl_2. Below 273 K, ISC, which is temperature independent, is the fastest process. These results are in good agreement with the Arrhenius parameters deduced as a function of temperature with other simple perfluoroarylnitrenes using product analysis.[1,8,16] It is important to note that the products isolated upon photolysis of perfluorophenyl azide change from those derived from ketenimine **8** to triplet nitrene **7T** at 273 K, in excellent agreement with time-resolved spectroscopic methods.[16]

Perfluorophenylnitrene. In our previous studies, it was not possible to resolve the formation of ylide **9** produced upon LFP of perfluorophenyl azide **6**.[8] However, following improvements in laser source, detection circuitry, and optics it became possible to resolve the growth of this ylide (Figure 9). The exponential growth of the ylide could be fit to yield an observed rate constant (k_{obs}). A plot of k_{obs} versus [pyridine] is linear (Figure 10). The slope at 294 K is $k_{pyr} = (5.8 \pm 0.8) \times 10^7\ M^{-1}\ s^{-1}$, the absolute rate constant of reaction of singlet nitrene **7S** with pyridine. The intercept of this plot is $1/\tau$, where τ is the lifetime of **7S** in the absence of pyridine (Table 2). Singlet perfluorophenylnitrene has a shorter lifetime (32 ns, 294 K) and reacts more rapidly with pyridine than does the perfluorobiphenyl analog. Arrhenius treatment of the absolute rate constant of reaction of **7S** with pyridine (k_{pyr}) is given in Figure 11 and yields $E_a = 1.66 \pm 0.16$ kcal/mol and $A = 10^{9.00\pm0.13}\ s^{-1}$.

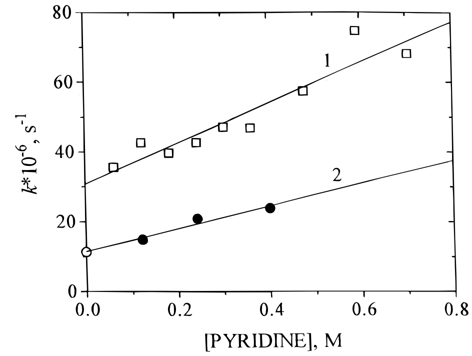


Figure 10. Plot of k_{obs} of ylide (**9**) formation versus [pyridine] following LFP (355 nm, Nd:YAG laser, 150 ps) of azide **6** in CH_2Cl_2: 1 (□, 294 K), 2 (●, 243 K).

TABLE 2: Data Obtained upon LFP (YAG Laser) of Azide 6 in CH_2Cl_2 (from plots such as Figure 10) by Monitoring the Formation of Ylide 9 as a Function of Pyridine

temp, °C	$k_{pyr} \times 10^{-7}$, $M^{-1}\ s^{-1}$	$k_{obs} \times 10^{-7}$, s^{-1}	τ, ns
22	6.2 ± 1.2	2.63	38
21	5.8 ± 0.8	3.08	32
−2		1.44	69
−6	4.3 ± 0.5	1.42	70
−19	3.4 ± 0.5	1.19	84
−26	3.4 ± 0.22	1.00	100
−28	3.6 ± 0.6		
−30.5	3.3 ± 0.4	1.17	86

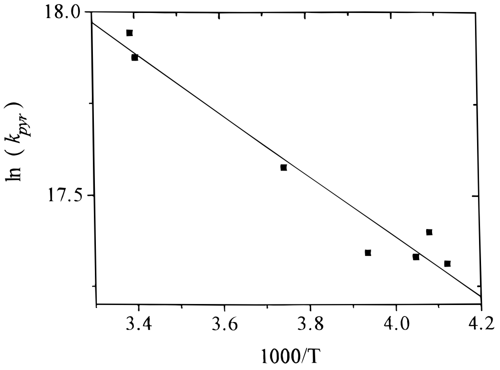


Figure 11. Arrhenius treatment of the data (k_{pyr}) of Table 2.

The lifetime of **7S** was measured as a function of temperature in CH_2Cl_2 using the pyridine ylide method. The shorter lifetime of **7S**, and its more limited temperature range, results in reduced precision relative to the biphenyl analog (Table 2, Figure 12).

It is also possible to observe the growth in transient absorption at 380 nm following LFP of **6**. The growth was exponential and could be fit to yield an observed rate constant ($k_{obs} = 1/\tau$, Figure 12). The absorption at 380 nm was mostly due to triplet nitrene **7T** (particularly below 273 K) but with some contribution of ketenimine **8** at the higher temperatures.

It was also possible to detect a rapidly decaying transient at 330 nm, following LFP (Nd:YAG laser, 10 mJ, 266 nm, 0.15 ns fwhm) of azide **6** in CH_2Cl_2 (Figure 13), attributed to singlet nitrene **7S**. A plot of $1/\tau$ determined by the three methods versus 1/*T* is given in Figure 12. Analysis of Figure 12 within

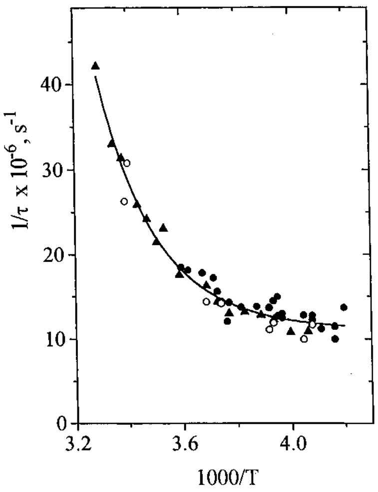


Figure 12. Plot of the rate constant of disappearance of perfluorophenyl singlet nitrene versus $1/T$: ○, data of the intercept of plots of ylide formation (390 nm) versus pyridine (LFP, Nd:YAG laser, 150 ps, at ambient temperature, 308 nm excimer laser, 15 ns, at temperatures below 0 °C); ●, direct measurement of triplet formation measured at 380 nm; ▲, data of the decay of transient absorption at 330 nm.

the context of Scheme 2 yields the following kinetic parameters.

$$1/\tau = k_{\mathrm{isc}} + k_{\mathrm{R}}$$

$$k_{\mathrm{isc}} = (1.05 \pm 0.05) \times 10^{7} \quad \mathrm{s}^{-1}$$

$$k_{\mathrm{R}} = 10^{13.8\pm0.13} \exp\left(-\frac{8800 \pm 400}{RT}\right) \quad \mathrm{s}^{-1}$$

III. Discussion

Absolute rate constants and Arrhenius parameters for the fundamental decay pathways of singlet perfluorophenylnitrene **7S** and singlet perfluoro-4-biphenylnitrene **13S** have been obtained by study of the decay of the singlet nitrene, the appearance of reaction products, and trapping with pyridine.

The spectra of the singlet nitrene intermediates closely resemble that of the lower energy triplet states of the nitrenes observed by low-temperature spectroscopy. This is consistent with calculations that indicate that the lowest singlet state of parent singlet phenylnitrene has an open-shell configuration as per the corresponding triplet.[7b,c]

The lifetimes of **7S** and **13S** are found to be 32 and 250 ns, respectively, in methylene chloride at ambient temperature. These lifetimes are very much longer than that of singlet arylcarbenes.[5] The lifetime of **13S** is 10 times longer than that of the intermediate produced upon LFP of 4,4′-biphenyl bisazide.[13] The slow rate of nitrene ISC is due to a large singlet−triplet gap and the open-shell nature of the lowest energy singlet configuration.[7] The shorter lifetime of **7S** is due mainly to a faster rate of ISC. It is difficult to identify the origin of this effect. Following Borden and Karney,[6] the slower rate of ISC of **13S** relative to **7S** may be a consequene of the increased delocalization of the electron in the π system of the biphenylnitrene. Perhaps this will reduce the spin−orbit coupling of the electrons in the singly occupied orbitals of the singlet and reduce the ISC rate.

The low intermolecular chemical reactivity of the singlet nitrenes is also a consequence of their open-shell configurations. This is evident in their absolute reactivity toward pyridine. Singlet nitrenes **7S** and **13S** react with pyridine about 100-fold more slowly than do arylcarbenes.[17]

On the other hand, arylnitrenes suffer intramolecular rearrangements much more rapidly than arylcarbenes which do not undergo this process in solution.[18] We have previously argued that this is due to the expectation that the π^2 configuration of arylnitrenes will rearrange readily and that this configuration is far more accessible than that electronic configuration of the arylcarbenes.[9] We have also argued that fluorine substituents destabilize the π^2 configuration and thereby retard the rate of rearrangement. The latter point has received some support from the calculations of Smith and Cramer,[19] but recent work of Borden and Karney[20] suggests that the fluorine effect may be steric in origin.

Borden and Karney's calculations[6] indicate that arylnitrenes expand to ketenimines by way of an azirine intermediate. Our data do not require that there be an intermediate in this reaction. However, our data are consistent with rate-determining cyclization of **7S** (and **13S)** to azirine **15** followed by rapid ring opening to ketenimine **8** (and **14**). The calculations of Borden and Karney indicate that the experimental values of k_{R} and its associated Arrhenius parameters should be related to azirine formation.

IV. Conclusion

Laser flash photolysis of perfluorophenyl azide and perfluoro-4-biphenyl azide produces singlet nitrenes which can be detected by their transient absorption. The kinetics of disappearance of the nitrenes was monitored by the disappearance of the nitrene absorption or the appearance of the absorption of the products. This has led to the following results in methylene chloride solvent.

singlet perfluoro-4-biphenylnitrene

$$k_{\mathrm{isc}} = (2.2 \pm 0.1) \times 10^{6} \quad \mathrm{s}^{-1}$$

$$k_{\mathrm{R}} = 10^{13.2\pm0.2} \exp\left(-\frac{9400 \pm 400}{RT}\right) \quad \mathrm{s}^{-1}$$

$$k_{\mathrm{pyr}} = 10^{9.06\pm0.15} \exp\left(-\frac{2400 \pm 200}{RT}\right) \quad \mathrm{M}^{-1}\,\mathrm{s}^{-1}$$

$$\tau(21\ {}^{\circ}\mathrm{C}) = 254 \pm 5 \quad \mathrm{ns}$$

singlet perfluorophenylnitrene

$$k_{\mathrm{isc}} = (1.05 \pm 0.05) \times 10^{7} \quad \mathrm{s}^{-1}$$

$$k_{\mathrm{R}} = 10^{13.8\pm0.3} \exp\left(-\frac{8800 \pm 400}{RT}\right) \quad \mathrm{s}^{-1}$$

$$k_{\mathrm{pyr}} = 10^{9.00\pm0.13} \exp\left(-\frac{1660 \pm 0.16}{RT}\right) \quad \mathrm{M}^{-1}\,\mathrm{s}^{-1}$$

$$\tau(21\ {}^{\circ}\mathrm{C}) = 32 \pm 3 \quad \mathrm{ns}$$

V. Experimental Section

Perfluorophenyl azide (**6**) was prepared by known procedures.[8]

Perfluoro-4-azidobiphenyl (12). A mixture of decafluorobiphenyl (1.07 g, 3.20 mmol) and hydrazine monohydrate (352 mg 7.03 mmol) in 1,4-dioxane (16 mL) was stirred under argon at ambient temperature for 12 h. The solvent was removed in vacuo, and the residue was neutralized with sodium bicarbonate (saturated), extracted with ether, dried ($MgSO_4$), and concentrated. The solid was dissolved in acetonitrile (20 mL), and concentrated HCl (2 mL) was added with stirring at 0 °C. The

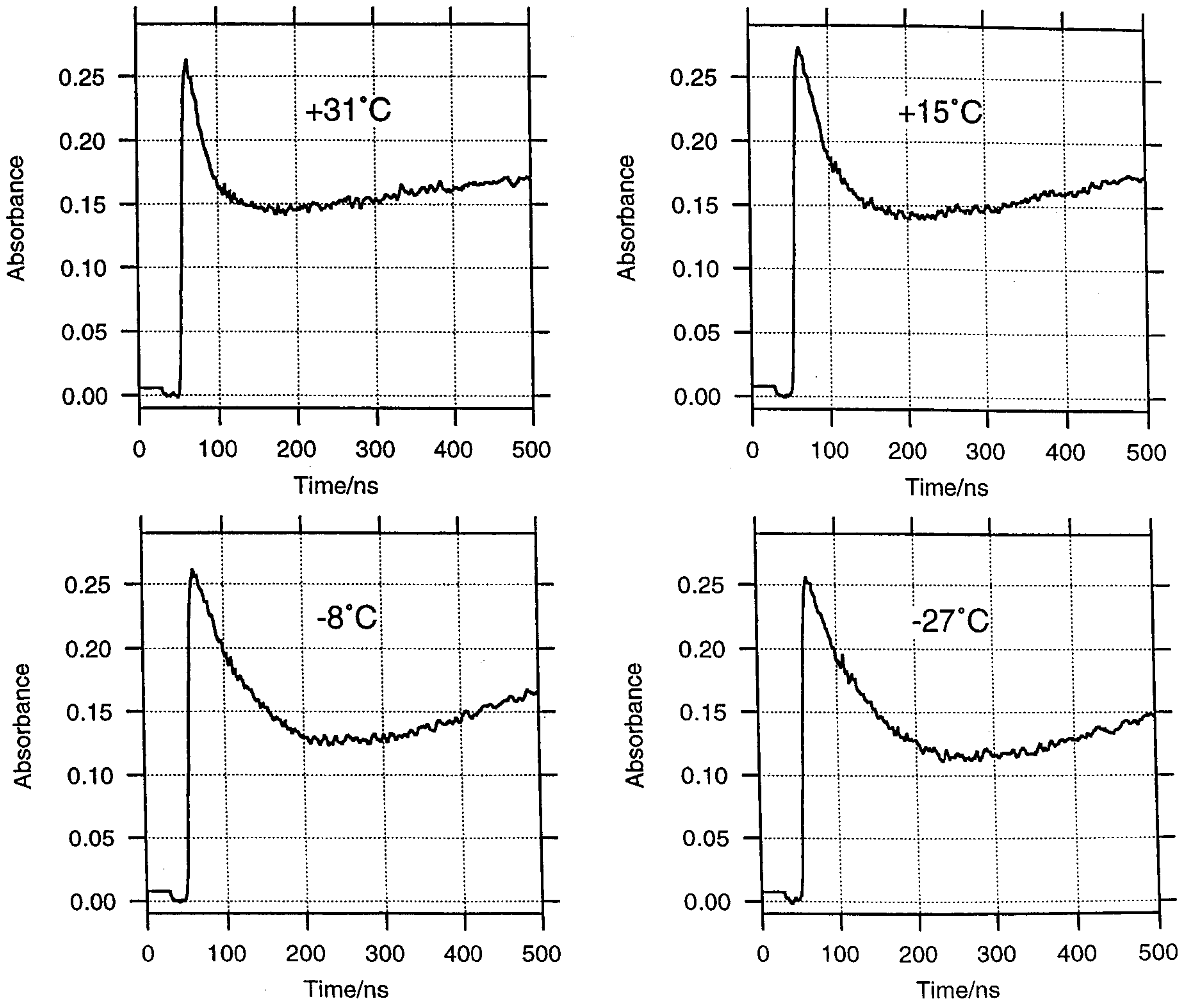


Figure 13. Rapidly decaying transient absorption (330 nm) following LFP (Nd:YAG laser, 266 nm, 150 ps) of **6** in CH_2Cl_2 as a function of temperature.

salt was collected on a sintered glass funnel and washed with ether. To a mixture of the salt obtained above in 5 N HCl (10 mL), water (400 mL), and ether (60 mL) was added dropwise a solution of sodium nitrite (486 mg, 7.04 mmol) in water (5 mL) while the temperature was maintained at 0−5 °C. The two layers were separated, and the aqueous layer was extracted with ether. The combined organic layers were washed with sodium bicarbonate (saturated) and water, dried ($MgSO_4$), and concentrated. The residue was chromatographed (neutral alumina (30 g), hexanes) to give 230 mg (21%) of perfluoro-4-azidobiphenyl as a yellowish solid after cooling in the freezer at −20 °C; mp 34−34.5 °C. ^{19}F NMR (250 MHz, $CDCl_3$): δ −161.97 (m, 2 F, 2 CF), −152.15 (m, 2 F, 2 CF), −151.57 (m, 1 F, CF), −139.51 (m, F, 2 CF), −138.77 (m, 2 F, 2 CF). IR (neat): ν 2172, 2122 cm^{-1}. MS (relative intensity): 357 (12, M^+), 329 (61, M − N_2), 310 (100, M − N_2 − F), 279 (40, M − N_2 − F − CF). High-resolution MS calculated for $C_{12}F_9N_3$ 356.9949; found 356.9948.

Laser Flash Photolysis. An excimer laser (Lambda Physik LPX105EMC, 308 nm, 15 ns) or Nd:YAG laser (Continium PY62C-10, 150 ps, 266 or 355 nm) was used as the excitation light source. The probe light of a pulsed xenon lamp was focused into a $^1/_4$ m grating monochromator (Oriel 77200) and detected with a photomultiplier tube (PMT). The PMT dynode chain is based on the design by Beck[21] modified by the addition of a 200 V Zener dynode to bias the first dynode and a nonlinear capacitor network to improve pulse response. The signal from the PMT (Hamamatsu, R928) was recorded with a digitizer (Tektronix 7912AD, 7A29 amplifier, 7B92A time base) and transferred to a personal computer. A typical solution was contained in a quartz cuvette and deoxygenated prior to photolysis by purging with argon. The sample solutions were changed after every laser shot in order to avoid effects due to the photoproduct.

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